

A Thermodynamic Model of Electric-Field-Induced Pattern Formation in Binary Dielectric Fluids

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Abstract

An electric-field-induced phase transition and pattern formation in a binary dielectric fluid layer are studied using a coarse-grained free energy functional. The electrostatic part of the free energy is a nonlinear functional of the dielectric function, which depends in turn on the local colloidal concentration. We determine the phase co-existence curve and find that beyond a critical electric field the system phase separates. Accompanying the phase separation are patterns similar to those observed in a spinodal decomposition of an ordinary binary fluid. The temporal evolution of the phase separating patterns are discussed both analytically and numerically by integrating a Cahn-Hilliard type of equation.

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I. INTRODUCTION

Systems undergoing a phase separation from a disordered phase to a more ordered state often form interesting patterns as they select and approach the final state[1]. The process of phase ordering, or coarsening dynamics, can be classified into different universality classes depending on the physical dimension, the dimension of the order parameter, and conservation laws[2, 3]. Typically the associated scaling properties and dynamical universalities can be understood using a coarse-grained free energy functional. A time-dependent Ginzburg-Landau approach then allows study of the evolving patterns.

Ferro-fluids[4], which are colloidal suspensions of magnetic particles in solution, exhibit complex labyrinthine pattern formation when trapped between closely spaced glass plates and subjected to a transverse magnetic field[4, 5, 6]. The complex patterns result from competition between the surface tension and long-range forces, and have much in common with patterns observed in amphiphilic systems and Langmuir-Blodgett films. In this paper we report on a similar effect in colloidal suspensions in which phase separation and a concomitant pattern formation are driven by an external electric field. Our results are based upon a macroscopic thermodynamic model of a dielectric binary liquid. This work was motivated by recent experiments demonstrating such behavior[7, 8], and shares some features in common with the experiments. We reported some preliminary results in Ref. 9.

We consider colloids consisting of nanometer scale (typical diameter ~ 10 nm) dielectric particles suspended in a dielectric solution. In the present work we are interested in patterns on length scales much larger than the particle size and the typical inter-particle spacing. Consequently we use a coarse-grained description similar to the model B used to study phase separation in binary liquids[2, 10]. For an order parameter we use the local particle concentration or volume fraction $c(\mathbf{r})$ ($0 \leq c \leq 1$). We model the particle interaction using a local dielectric constant $\varepsilon(c(\mathbf{r}))$ which depends nonlinearly on the local concentration. The use of a phenomenological dielectric constant with a positive curvature is an important ingredient of the model. It turns out that beyond a critical value of the electric field the electrostatic energy dominates and drives phase separation and pattern formation.

The approach developed in this paper is thermodynamic, based on a macroscopic free

energy. Analyzing equilibrium properties yields a phase diagram which exhibits instabilities that can lead to pattern formation. Some understanding of the dynamics of pattern formation then comes from investigating the corresponding time dependent Ginzburg-Landau equation. We begin by describing the model free energy and its equilibrium properties, and then turn to dynamics.

II. MODEL FREE ENERGY

Consider a binary dielectric liquid as described above placed between parallel capacitor plates separated by d . The liquid has capacitance

$$C = \frac{1}{4\pi d^2} \int d^3r \, \varepsilon(c(\mathbf{r})). \quad (1)$$

When the internal energy is dominated by the electrostatic contribution, the Helmholtz free energy is

$$F = \frac{1}{2}QV - TS, \quad (2)$$

where V is the voltage between the plates, T the temperature, and S the entropy. The equilibrium state is obtained by minimizing F at constant Q, T . For our purposes it is more convenient to make a Legendre transformation to a different free energy:

$$\Omega = F - QV = -\frac{1}{2}QV - TS. \quad (3)$$

Equilibrium is found by minimizing Ω at constant V, T (note that V is voltage and not volume). We will refer to Ω as “the” free energy.

For the dielectric constant ε we use a phenomenological model due to Lichteneker[8, 11]:

$$\varepsilon(c) = \varepsilon_f e^{\gamma c}, \text{ where } \gamma = \ln \varepsilon_p / \varepsilon_f. \quad (4)$$

This interpolates between the dielectric constant of pure solvent (ε_f) and that of pure particle (ε_p) as the concentration varies from $c = 0$ to $c = 1$. In this paper we use a physically reasonable value $\gamma = 3$ [7, 8]. The specific choice of $\varepsilon(c)$ in Eq. (4) is not essential. The results we report turn out to be largely independent of the form of $\varepsilon(c)$, as long as it has positive curvature (a point we discuss later).

We use an approximate entropy functional appropriate for interacting particles at low concentration [7, 8, 12, 13]:

$$S = -\frac{k_B}{v} \int d^3r [c(\mathbf{r}) \ln c(\mathbf{r}) + (1 - c(\mathbf{r})) \ln(1 - c(\mathbf{r}))]. \quad (5)$$

This expression can be obtained by a simple counting argument. In the absence of interactions v is the particle volume and Eq. (5) is the entropy of free particles [14]. Here however v is instead the so-called ‘correlation volume,’ which accounts phenomenologically for the particle interactions.

In a typical experiment the plate separation d is so small that the concentration $c(\mathbf{r})$ can be treated as effectively two-dimensional. Then we can let the coordinate $\mathbf{r} = (x, y)$ denote lateral position within the plane. In this limit the electric field E becomes uniform ($E = V/d$), and the free energy becomes

$$\Omega = d \int d^2r f(c(\mathbf{r})), \quad \text{where} \quad (6a)$$

$$f(c) = -\frac{E^2}{8\pi} \varepsilon(c) + \frac{k_B T}{v} [c \ln c + (1 - c) \ln(1 - c)]. \quad (6b)$$

For $\varepsilon(c)$ given in Eq. (4), the temperature and electric field naturally scale to the dimensionless form

$$\tilde{T} = \frac{k_B T / v}{\varepsilon_f E^2 / 8\pi}. \quad (7)$$

III. EQUILIBRIUM PHASE SEPARATION

We are interested in potential phase separations in the system. These can occur if $f(c)$ possesses inflection points[15]. Suppose that in equilibrium the system phase separates into volume fractions $x_{1,2}$ with concentrations $c_{1,2}$. If the average concentration is c , then these must satisfy

$$\sum_{i=1}^2 x_i = 1, \quad \sum_{i=1}^2 x_i c_i = c, \quad (8)$$

and so

$$x_1 = \frac{c_2 - c}{c_2 - c_1}, \quad x_2 = \frac{c - c_1}{c_2 - c_1}. \quad (9)$$

To find the conditions under which the equilibrium state is phase-separated in this manner, we minimize the free energy $\sum_i x_i f(c_i)$ with respect to c_1, c_2, x_1, x_2 , subject to the constraints Eq. (8). Using Lagrange multipliers, this means minimizing

$$\tilde{\Omega} = \sum_{i=1}^2 x_i [f(c_i) - \mu c_i - \lambda]. \quad (10)$$

Except at the endpoints (x_i or c_i equal to 0 or 1) this minimization yields

$$f(c_i) = \mu c_i + \lambda \quad (11a)$$

$$f'(c_i) = \mu. \quad (11b)$$

If c_1 and c_2 both satisfy Eq. (11a), then

$$f(c_2) - f(c_1) = \mu(c_2 - c_1). \quad (12)$$

This result is summarized by a simple geometrical construction illustrated in Fig. 1. If the straight line joining the points $(c_1, f(c_1))$ and $(c_2, f(c_2))$ is tangent to $f(c)$ at both points, then phase separation will occur for $c_1 \leq c \leq c_2$. This can occur only if $f(c)$ has two or more inflection points (see Fig. 1). For our model, the endpoints $c = 0, 1$ never correspond to a minimum free-energy state.

Consider now the free energy density $f(c)$ for our dielectric fluid, Eq. (6b). The entropic term $-TS$ has positive curvature. At high temperatures this term dominates, $f(c)$ has positive curvature everywhere, and the equilibrium state is homogeneous. This is illustrated by the highest-temperature trace ($\tilde{T} = 20$) in Fig. 2, which uses the model dielectric function Eq. (4). As the temperature is lowered the electrostatic energy term $-QV/2 = -E^2 \varepsilon(c)/8\pi$ plays an increasingly important role. When $\varepsilon(c)$ has positive curvature, the electrostatic term has negative curvature, and at low temperatures this term leads to inflection points and phase separation. This is illustrated by the two lower-temperature traces in Fig. 2.

The phase diagram for the free energy Eq. (6b), developed using the above procedure, is shown in Fig. 3 for $\gamma = 3$. Below the coexistence curve (the solid line) the homogeneous phase becomes metastable and in equilibrium the system phase-separates. This curve is the locus of points $c_{1,2}$ obtained from solving Eq. (11) at all temperatures. Although there is no

exact expression for the coexistence temperature, for the physically important case of low concentrations we find approximately

$$\tilde{T}_{\text{coex}} \approx \frac{(1 + \gamma - \gamma c)e^{\gamma c} - e^{\gamma}}{\ln c}. \quad (13)$$

For $\gamma = 3$ this is accurate for concentrations $c \lesssim 0.3$.

Lying below the dashed phase boundary in Fig. 3 is the classical spinodal region, where the homogeneous state becomes unstable [$f''(c) < 0$]. This phase boundary is given by the condition $f''(c) = 0$, which yields

$$\tilde{T}_s = \gamma^2 e^{\gamma c} c(1 - c). \quad (14)$$

The coexistence and spinodal curves touch at a critical point (marked by a diamond in Fig. 3). This occurs at the critical concentration c_c and critical temperature T_c where the two inflection points present at lower temperatures coincide [and so $f''(c_c) = 0 = f'''(c_c)$]. For the model dielectric function Eq. (4) the critical values are:

$$c_c = \frac{1}{2\gamma} \left(\gamma - 2 + \sqrt{\gamma^2 + 4} \right) \quad (15a)$$

$$\tilde{T}_c = \gamma^2 e^{\gamma c_c} c_c(1 - c_c). \quad (15b)$$

The instabilities give the possibility of pattern formation, which we now discuss.

IV. PATTERN FORMATION: DYNAMICS

Pattern formation after quenches into the metastable or spinodal regions provides important insight into the underlying mechanisms for phase transformation in the system. For a system like the one modeled here it is experimentally easier to increase the voltage suddenly while holding the temperature fixed; by Eq. (7) this is equivalent to a quench. Here we investigate pattern formation under quenches using a phenomenological diffusion equation developed from the free energy.

Notice first that when inhomogeneities arise the free energy needs an additional $|\nabla c|^2$ term. This can be viewed as the surface energy between domains of different concentration;

such terms arise generally in any interacting system. Consequently in this section we write the free energy

$$\Omega = \int d^3r \left[f(c(\mathbf{r})) + \frac{1}{2}\kappa |\nabla c|^2 \right], \quad (16)$$

where κ is a phenomenological parameter.

Fick's law relates the concentration current density to the local chemical potential μ :

$$\mathbf{j}(\mathbf{r}) = -Mv_0 \nabla \mu(\mathbf{r}), \quad (17)$$

where M is the mobility (taken to be constant) and v_0 is the volume of the colloidal particle. Combining this with the continuity equation $\dot{c} + \nabla \cdot \mathbf{j} = 0$ yields a diffusion equation

$$\frac{\partial c}{\partial t} = Mv_0 \nabla^2 \mu. \quad (18)$$

The local chemical potential is obtained from the free energy:

$$\mu(\mathbf{r}) = v_0 \left. \frac{\delta \Omega}{\delta c(\mathbf{r})} \right|_{TE} = v_0 [f'(c(\mathbf{r})) - \kappa \nabla^2 c(\mathbf{r})]. \quad (19)$$

Inserting this into Eq. (18) gives

$$\frac{\partial c}{\partial t} = Mv_0^2 [\nabla^2 f'(c(\mathbf{r})) - \kappa \nabla^4 c(\mathbf{r})]. \quad (20)$$

The free energy density $f(c)$ is in Eqs. (6b,4). A convenient dimensionless form comes from writing time in units of τ and length in units of λ , where

$$\tau = \frac{\kappa}{Mv_0^2} \left(\frac{8\pi}{\varepsilon_f E^2} \right)^2 \quad (21a)$$

$$\lambda = \sqrt{\frac{8\pi\kappa}{\varepsilon_f E^2}}. \quad (21b)$$

Then the diffusion equation becomes

$$\frac{\partial c}{\partial t} = \nabla^2 [\tilde{f}'(c) - \nabla^2 c], \quad (22a)$$

where

$$\tilde{f}(c) = -e^{\gamma c} + \tilde{T} [c \ln c + (1-c) \ln(1-c)]. \quad (22b)$$

Eq. (22a) is nothing but the time-dependent Ginzburg-Landau equation for a scalar conserved order parameter; however, the free energy in this particular case is constructed with the parameters directly relevant to experiments on dielectric colloidal fluids[7, 8]. We study pattern formation after quenches by solving this nonlinear diffusion equation, starting from a uniform distribution (plus a small random component).

One can get some intuition about dynamics by linearizing the diffusion equation[2]. The result is accurate for early times, before the nonlinear terms become significant. Write $c(\mathbf{r}) = c + \delta c(\mathbf{r})$, where c is the average concentration. For small δc expand

$$\tilde{f}(c + \delta c) = \tilde{f}(c) + \tilde{\mu}_0 \delta c - \frac{1}{2} b (\delta c)^2 + \dots, \quad (23)$$

where

$$\tilde{\mu}_0 = \tilde{f}'(c) = -\gamma e^{\gamma c} + \tilde{T} [\ln c - \ln(1 - c)] \quad (24a)$$

$$b = -\tilde{f}''(c) = \frac{\tilde{T}_s - \tilde{T}}{c(1 - c)}. \quad (24b)$$

\tilde{T}_s is given in Eq. (14). The linear and constant terms in Eq. (23) play no role in the dynamics. Keeping only the second order term from Eq. (23), the free energy Eq. (16) becomes

$$\Omega \approx \frac{1}{2} \int d^3r [\kappa |\nabla \delta c|^2 - b (\delta c)^2]. \quad (25)$$

This expansion connects our model to the coarsening dynamics of a binary alloy described by a conserved scalar order parameter $\phi(\mathbf{r})$. The free energy for such a system is generally assumed to have the Ginzburg-Landau form

$$F = \frac{1}{2} \int d^3r [\kappa |\nabla \phi|^2 - b \phi^2 + \frac{u}{2} \phi^4] \quad (26)$$

where κ , and u are assumed to be positive. Below the critical temperature b becomes positive, yielding a broken symmetry. Higher-order terms beyond ϕ^4 are irrelevant for the dynamic universality class. In fact, the early-time dynamics are dominated by ϕ^2 terms. From the correspondence between Eqs. (25), (26) we expect our model to have early-time dynamics very similar to those of model B.

Using the expansion Eq. (25) linearizes the diffusion equation Eq. (22):

$$\frac{\partial(\delta c)}{\partial t} = -\nabla^2 [b \delta c + \nabla^2 \delta c]. \quad (27)$$

This is solved by expanding the fluctuation δc in Fourier components:

$$\delta c(\mathbf{r}, t) = \int \frac{d^2 k}{(2\pi)^2} e^{i\mathbf{k} \cdot \mathbf{r}} c(\mathbf{k}, t). \quad (28)$$

We find

$$c(\mathbf{k}, t) = c(\mathbf{k}, 0) e^{\alpha_k t}, \text{ where } \alpha_k = k^2(b - k^2). \quad (29)$$

Outside of the spinodal region $\tilde{T} > \tilde{T}_s$ and so by Eq. (24b) $b < 0$. Consequently all components $c(\mathbf{k}, t)$ decay. This describes the homogeneous equilibrium state: fluctuations away from a uniform concentration decay.

However, within the classical spinodal region $b > 0$. Thus long wavelength modes, those with wave vector $k < \sqrt{b}$, grow exponentially. The most rapid growth occurs for $k_m = \sqrt{b/2}$, where α_k reaches its maximum value $b^2/4$. Thus in the classical spinodal regime, where the homogeneous state is unstable, early-time exponential growth leads to structures a typical (dimensionless) length scale $k_m^{-1} \sim (\tilde{T}_s - T)^{-1/2}$. These structures grow exponentially in time with a (dimensionless) time scale $1/\alpha_{k_m} = 4/b^2 \sim (\tilde{T}_s - \tilde{T})^{-2}$.

For example, consider the structure factor

$$S(\mathbf{k}, t) = \langle c(\mathbf{k}, t) c(-\mathbf{k}, t) \rangle. \quad (30)$$

Here angle brackets represent a statistical average. Suppose that the initial fluctuations $c(\mathbf{k}, 0)$ are small and uncorrelated:

$$\langle c(\mathbf{k}, 0) c(\mathbf{k}', 0) \rangle = A^2 \delta^2(\mathbf{q} - \mathbf{q}'). \quad (31)$$

Then for early times

$$S(\mathbf{k}, t) = A^2 e^{2\alpha_k t}. \quad (32)$$

This grows ever more peaked at k_m as time increases. Fourier transforming gives the real-space correlation function

$$\langle \delta c(\mathbf{r}, t) \delta c(\mathbf{r}', t) \rangle \sim \frac{A^2}{t^{1/2}} e^{b^2 t/4} J_0(k_m |\mathbf{r} - \mathbf{r}'|) \quad (33)$$

which exhibits the length and time scales described above.

Including dimensions, the structures developing in early times have a length scale

$$L \sim \frac{\lambda}{k_m} = \sqrt{\frac{8\pi\kappa}{\varepsilon_f E^2}} \sqrt{\frac{2c(1-c)}{\tilde{T}_s - \tilde{T}}} = \sqrt{\frac{2c(1-c)k_B/v}{T_s - T}} \quad (34)$$

and grow with a time scale

$$t_0 \sim \frac{4\tau}{b^2} = \frac{\kappa}{Mv_0^2} \left(\frac{8\pi}{\varepsilon_f E^2} \right)^2 \left[\frac{2c(1-c)}{\tilde{T} - \tilde{T}_s} \right]^2 = \frac{\kappa}{Mv_0^2} \left[\frac{2c(1-c)k_B/v}{T - T_s} \right]^2. \quad (35)$$

Deep quenches into the classical spinodal region should lead to dynamically-developing structures on a length scale L given by Eq. (34). These structures result from a long-wavelength instability. They represent not the equilibrium state, but the early-time evolution from the highly non-equilibrium homogeneous state toward the (eventual) phase-separated equilibrium. The linearized description is accurate for very small initial times. Soon the fluctuations grow large enough for the nonlinear terms to play a role, and we turn to numerical means for the solution of Eq. (22).

V. NUMERICAL INTEGRATION OF THE DIFFUSION EQUATION

We numerically integrate the lattice discretized version of Eqs. (22) using a first-order Euler scheme, choosing step sizes to avoid unphysical instabilities[16]. This algorithm is adequate for times during which the system begins to organize into patterns. To carry the simulation all the way to phase separation requires a more sophisticated approach[17]. However the model we use also omits hydrodynamic effects which may be important for the late time coarsening process. Consequently here we present results during the era of pattern formation only.

The initial configuration consists of a uniform concentration c plus a small random component. Starting from this initial state, Eq. (22) is integrated for various values of γ and \tilde{T} . In agreement with the results of the previous sections we find that phase separation occurs below the coexistence temperature \tilde{T}_{coex} (or, equivalently, above a threshold electric field). In the phase-separation region the concentration develops labyrinthine patterns consisting of stripes of higher and lower concentration.

Typical results for a quench deep into the phase separation region are shown in Figs. 4 and 5. The latter clearly shows that a labyrinthine pattern has developed.

We monitor two quantities during the simulation. At each time step we search for the maximum and minimum concentrations, and define a contrast parameter $(c_{\max} - c_{\min})/2c$. This parameter indicates the visibility of the developing pattern. Another quantity of interest is the pair correlation function

$$G(\vec{r}, t) = \left\langle \frac{1}{V} \int (c(\vec{r}, t) - c)(c(\vec{r} + \vec{r}', t) - c) d^2\vec{r}' \right\rangle. \quad (36)$$

The average domain width R_g can be calculated from the first zero of the normalized pair correlation function $\tilde{G}(\vec{r}, t) = G(\vec{r}, t)/G(0, t)$. The upper panel of Fig. 4 shows the early time variation of the contrast parameter and the domain width R_g as a function of the scaled time. The average domain width after a rapid initial increase saturates at this temperature to a value $\sim 4.5\lambda$.

VI. SUMMARY

We have studied the electric-field-induced phase separation of a dielectric binary fluid using a coarse-grained free energy functional. The free energy investigated is guided by experiments on field-driven instabilities in ferro-colloids, and shares features of a Ginzburg-Landau free energy that describes the phase separation of a binary mixture. Certain other features of ferro-particles which would require a more complicated order parameter have been omitted, *e.g.* the orientational ordering arising from the magnetic dipolar interaction.

The first order co-existence curve of the model clearly shows how a spinodal decomposition can be driven by an electric field in colloidal systems. Analytical estimates of the critical field are consistent with the numerical results. Deep quenches show a typical labyrinthine pattern formation with characteristic length and time scales set by the free energy.

The phenomenology used here is most accurate at low particle concentrations. In particular, the entropy is essentially that of free particles, modified to take interactions into account *via* the phenomenological correlation volume v . The resulting entropy is at least

qualitatively correct at low concentrations but not high. Experiments with low overall concentrations should be described with reasonably accuracy by this model.

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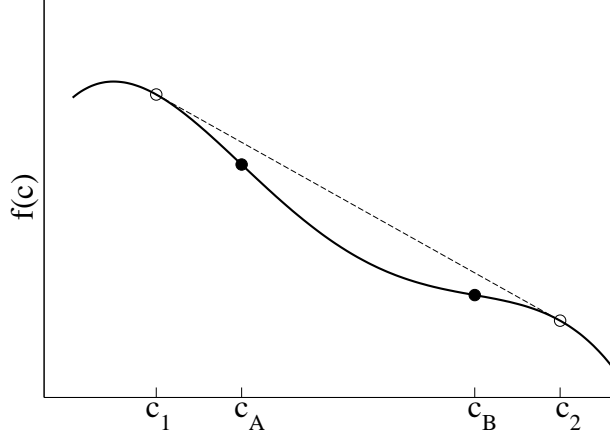


FIG. 1: Two points on a curve can have a common tangent only if the curve has at least two inflection points. The inflection points at c_A, c_B are indicated by filled circles and the phase separation points at c_1, c_2 by open circles.

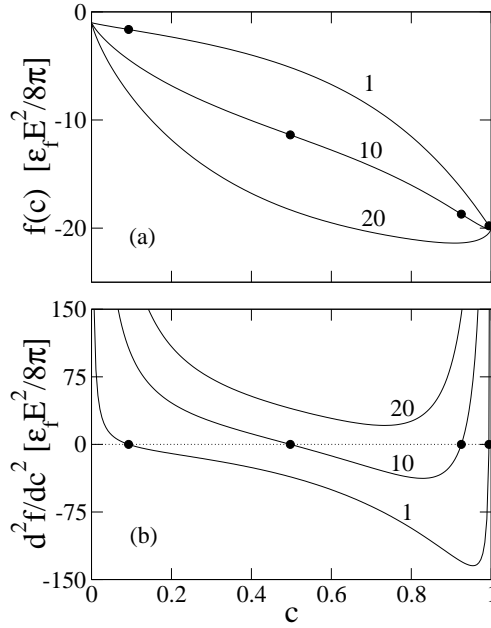


FIG. 2: (a) $f(c)$ vs. c for the three scaled temperatures $\tilde{T} = 1, 10, 20$, using Eqs. (6b,4) with $\gamma = 3$. At the two lower temperatures two inflection points are present. These are more easily seen in (b) $f''(c)$ vs. c . The inflection points are indicated by filled circles.

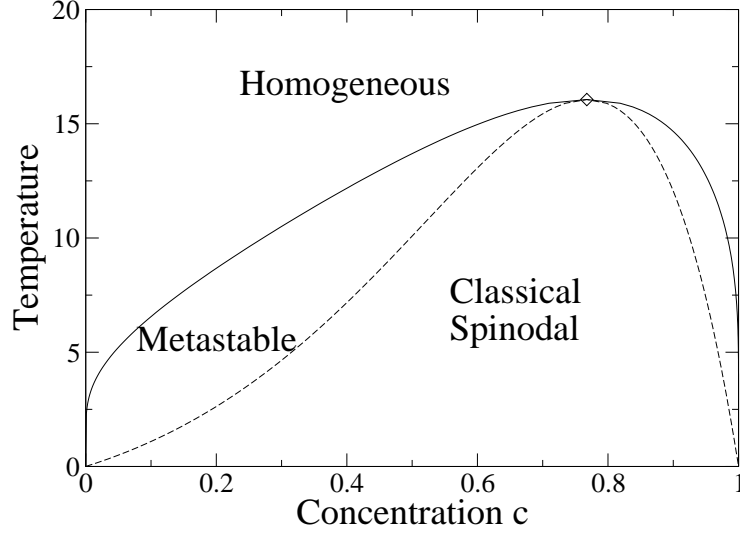


FIG. 3: Phase diagram for the free energy given in Eqs. (6b,4) for $\gamma = 3$. Temperature is \tilde{T} . Shown are the coexistence curve \tilde{T}_{coex} (solid) and the spinodal \tilde{T}_s (dashed). The critical point Eq. (15) is marked by a diamond.

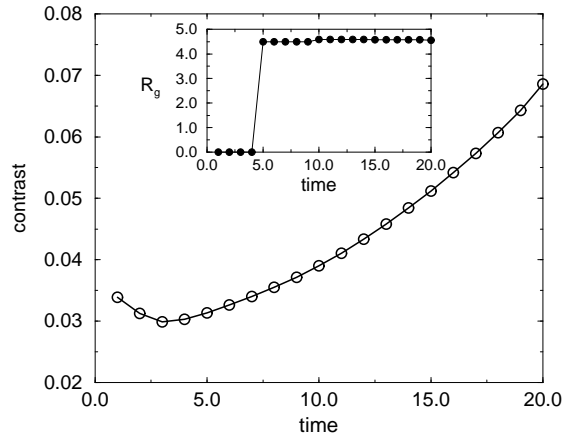


FIG. 4: Early stage increase in contrast $(c_{\text{max}} - c_{\text{min}})/2c$ and domain size (inset) as a function of time. Here time and space are in the units of Eq. (21). The simulation was done on a 128×128 lattice with an initial random configuration ± 0.01 around $c = 0.1$ for $\gamma = 1.0$ and $\tilde{T} = 0.045$.

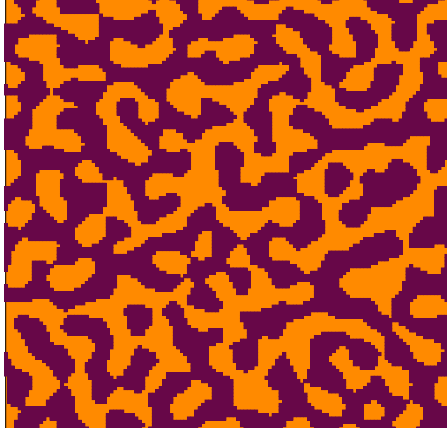


FIG. 5: A typical snapshot at time 20. Concentrations greater (less) than the average c are dark (light).